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(21) International Application Number: PCT/KR99/00407 (22) International Filing Date: 27 July 1999 (27.07.99) (30) Priority Data: 1998/30208 27 July 1998 (27.07.98) KR (71) Applicant (for all designated States except US): LG CHEMICAL LTD. [KR/KR]; LG Twin Towers, Youido-dong, 20, Yongsungpo-ku, Seoul 150-721 (KR). (72) Inventors; and (75) Inventors/Applicants (for US only): KIM, Dong-Il [KR/KR]; Songgang-Green Apt., 316-701, Songgang-dong, Yuseong-ku, Daejeon-city 305-503 (KR). KIM, Tae-Seong [KR/KR]; Sejong Apt., 102-203, Jeonmin-dong, Yuseong-ku, Daejeon-city 305-390 (KR). RANG, Moon-Jeong [KR/KR]; Sejong Apt., 108-606, Jeonmin-dong, Yuseong-ku, Daejeon-city 305-390 (KR). (74) Agent: KIM, Won-Ho; 702, Teheran Bd., 825-33, Yoksam-dong, Kangnam-ku, Seoul 135-080 (KR).		(81) Designated States: CN, ID, IN, JP, US, VN, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: PREPARATION OF CATIONIC SURFACTANTS CONTAINING ESTER GROUP IN MOLECULES		
<div style="text-align: center;"> $\left[\begin{array}{c} R^1 \\ \diagup \\ N^+ \\ \diagdown \\ R^1 \end{array} \begin{array}{c} (CH_2)_n - A \\ CH_2CHCH_2OCR^2 \\ \quad \quad \\ OH \quad \quad O \end{array} \right] X^- \quad (1)$ </div>		
(57) Abstract <p>The present invention relates to a method for preparing a cationic surfactant in which physical chemical characteristics such as softness, antistatic properties, etc. as well as biodegradability are quite excellent due to having an ester group and a hydrophilic hydroxyl group in its molecules. A cationic surfactant of the present invention is prepared by reacting tertiary amine derivatives, fatty acid, and epihalohydrin, and prepared simply by reacting esterification and quaternary reactions in one step with a high yield. The above cationic surfactant is a high grade alkyl quaternary ammonium compound as represented in General Formula (1), wherein R¹ is a C₁ - C₄ alkyl group; R² is a C₇ - C₂₁ linear or branched alkyl or alkenyl group; A is OCOR³, NHCOR³ or OH; R³ is a C₇ - C₂₁ linear or branched alkyl or alkenyl group; X is a halogen atom; and n is an integral number from 2 to 6.</p>		

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PREPARATION OF CATIONIC SURFACTANTS CONTAINING ESTER GROUP IN MOLECULES

CROSS REFERENCE TO RELATED APPLICATION

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This application is based on application No. 98-30208 filed in the Korean Industrial Property Office on July 27, 1998, the content of which is incorporated hereinto by reference.

BACKGROUND OF THE INVENTION

10 (a) Field of the Invention

The present invention relates to a method for preparing a cationic surfactant, and more particularly to a method for preparing a new cationic surfactant in which an esterification reaction of a fatty acid and a quaternary reaction of tertiary amine are progressed simultaneously and in a simple
15 method so that an ester group and a hydroxyl group exist in the molecules resulting in excellent biodegradability and solubility in water.

(b) Description of the Related Art

A cationic surfactant, the hydrophilic radical portion of which is dissociated as a cation when dissolved in water, has a structure that is
20 opposite to that of an anionic surfactant (fatty acid soap) such that it is also called an invert soap. A cationic surfactant is not only applied to produce ordinary surface activity effects such as rinsing, emulsification, solubilization, etc., but also displays softening and antistatic effects. A cationic surfactant is classified as a quaternary ammonium compound or an amine derivative
25 depending on its structure.

Although dimethyl dialkyl ammonium chloride (DDAC) has been typically used as a representative cationic surfactant, its consumption has been decreased more and more due to the low biodegradability of DDAC.

Therefore, studies related to injecting a group having a biodegradable functional group (such as ester or amide in an alkyl group) into molecules are actively being pursued.

Among the different types of cationic surfactants developed in this manner, quaternary ammonium compound of amidoamine, quaternary ammonium compound of amidoesteramine, imidazoline, and imidazoline ester based cationic surfactants are most commonly used. Examples include an amidoamine compound, and a preparing method and a softener of cationic surfactants using this compound disclosed in Japanese Patent No. Heisei 6-345704; an amidoesteramine compound, and a preparing method and a softener of cationic surfactants using this compound disclosed in Japanese Patent No. Heisei 6-336466; a softener composition containing imidazoline ester disclosed in Japanese Patent No. Heisei 4-257372; and a method for preparing a conditioning compound containing imidazoline disclosed in Japanese Patent No. Heisei 2-1479.

Nevertheless, a wide range of studies to develop cationic surfactants with excellent biodegradability are still being pursued since the biodegradability of the above patents is low despite the improvement over the biodegradability of DDAC. As a result of such research, it has been determined that if an alkyl group, which is a lipophilic part in molecules of a cationic surfactant, includes an easily degradable functional group like an ester group, its biodegradability becomes quite excellent compared with conventional dimethyl dialkyl ammonium chloride, amide based quaternary ammonium compound, and imidazoline based cationic surfactant (Tenside Surfactant Detergent, 1993, 30, 186-191).

Accordingly, various derivatives of quaternary ammonium compound having an ester group in molecules thereof are being widely studied. Typical examples, which have been commercialized, include WO 94-07978 in which a softener and a hair care product were prepared using a cationic surfactant derived from triethanol amine; WO 93/23510 in which a concentrated fabric softener and a biodegradable fabric softener composition were prepared using

a cationic surfactant having ester group at two hydrophobic groups; and WO 92/15745 in which a concentrated fabric softener composition was prepared using linear fatty alcohol ethoxylate and polydialkylsiloxane, etc., in imidazoline or imidazoline ester. A concentrated fabric softening and dispersing agent comprising a quaternary ammonium compound prepared from triethanol amine and fatty acid was prepared in WO 94/14935, and a concentrated fabric softener was prepared using a small amount of a quaternary ammonium compound having an ester group in molecules (and a nonionic dispersing agent) in WO 94/13772.

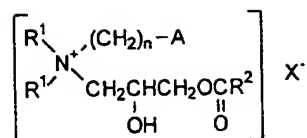
However, in case of the molecules containing the above quaternary ammonium compound with an ester group, solubility in water is so low that the inherent basic properties of the quaternary ammonium compound are deteriorated when large amounts of compounds such as glycerin based, low grade alcohols and nonionic dispersing agents are used in order to maintain the long-term stability of the salt. Further, although the biodegradability of this quaternary ammonium compound has considerably been improved over the existing dimethyl dialkyl ammonium chloride (DDAC), there are still improvements required in this respect.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method for preparing a cationic surfactant which maintains excellent softening and antistatic properties associated with quaternary ammonium compound characteristics while having a low toxicity, is and highly biodegradable as a result of having a group in its molecules, and also has excellent dispersing properties in water due to its superior solubility in water.

To achieve the above object, the present invention provides a method for preparing a cationic surfactant of the following General Formula 1 prepared by reacting tertiary amine derivatives, epihalohydrin, and fatty acids:

[General Formula 1]



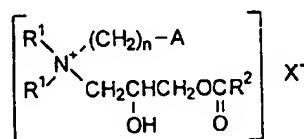
wherein R¹ is a C₁ – C₄ alkyl group; R² is a C₇ – C₂₁ linear or branched alkyl or alkenyl group; A is OCOR³, NHCOR³ or OH; R³ is a C₇ – C₂₁ linear or branched alkyl or alkenyl group; X is a halogen atom; and n is an integral number from 2 to 6.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will now be described in detail. As will be realized, the invention is capable of modification in various obvious respects, all without departing from the invention. Accordingly, the description is to be regarded as illustrative in nature, and not restrictive.

The present invention is characterized in that a cationic surfactant of the following General Formula 1 is prepared by performing an esterification reaction together with a quaternary reaction without catalysts using reactants of tertiary amine derivatives, fatty acids, and epihalohydrin:

[General Formula 1]

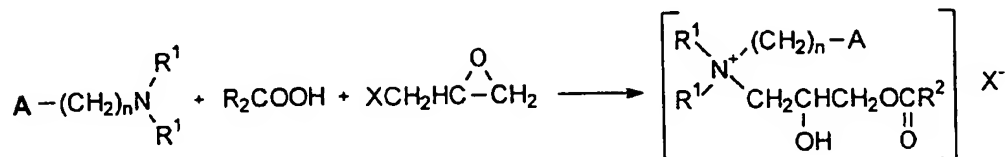


wherein R¹ is a C₁ – C₄ alkyl group; R² is a C₇ – C₂₁ linear or branched alkyl or alkenyl group; A is OCOR³, NHCOR³ or OH; R³ is C₇ – C₂₁ linear or branched alkyl or alkenyl group; X is a halogen atom; and n is an integral number from 2 to 6.

A cationic surfactant of the present invention is readily biodegradable while maintaining the inherent properties of quaternary ammonium compounds, i.e., softness, antistatic properties, etc. at least equal to levels in conventional quaternary ammonium compounds, as well as containing an ester group. Furthermore, it has improved solubilities in water by employing hydrophilic parts in the molecules of the compounds.

The preparing process of this cationic surfactant is represented in the following Reaction Formula 1:

[Reaction Formula 1]

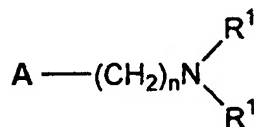


5 wherein R^1 , R^2 , A , R^3 , X , and n are the same as in the above General Formula 1.

In the above Reaction Formula, when tertiary amine derivatives, fatty acids, and epihalohydrin are reacted simultaneously, the epihalohydrin and fatty acids are reacted to form an alkyl halide having ester group with the tertiary amine derivative acting as a catalyst. The resulting material is again
10 reacted with tertiary amine derivative resulting in a formation of quaternary ammonium compound.

The above tertiary amine derivative is represented as in the following General Formula 2:

15 [General Formula 2]



wherein R^1 is a $C_1 - C_4$ alkyl group; A is $OCOR^3$, $NHCOR^3$ or OH ; R^3 is a $C_7 - C_{21}$ linear or branched alkyl or alkenyl group; and n is an integral number from 2 to 6.

20 The above tertiary amine derivatives are amide or tertiary amine containing ester groups which are synthesized by reacting dialkyl amino alkyl amine or dialkyl hydroxyalkyl amine derivatives with fatty acids. During the synthesis, it is preferable that the reaction temperature is 100 to 200°C, the reaction pressure is 1 to 10 atmospheres, and the reaction time is 3 to 20
25 hours. In case that the tertiary amine containing ester groups are prepared, a

catalyst can selectively be used. The usable catalysts are phosphoric acid, hypophosphorous acid, p-toluene sulfonic acid, hydrochloric acid, etc. The consumed amount of the usable catalysts is 0.01 to 1.0 wt% of the total reactant amount.

5 A mixture of more than one or two fatty acids having a $C_8 - C_{22}$ linear or branched alkyl or alkenyl group can be used as the above fatty acid. Examples include octanoic acid, decanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, octadecanoic acid, eicosanoic acid, and docosanoic acid. The fatty acids have an equivalent of 0.8 to 1.3 of
10 tertiary amine derivatives. A drawback of the formation of an insufficient amount of the target material occurs when the consumed amount of fatty acid has an equivalent of less than 0.8 in the tertiary amine derivatives. When this equivalent is over 1.3, non-reacted fatty acid and alkyl halide having ester group remain, deteriorating physical properties.

15 The above epihalohydrin uses an equivalent of 1.0 to 1.3, preferably 1.0 to 1.1, in the tertiary amine derivative. The drawbacks of an increase in toxicity and a deterioration in physical properties occur as a result of the existence of non-reacted tertiary amine when the equivalent of epihalohydrin is less than 1.0 in the tertiary amine. When this equivalent is over 1.3, an
20 insufficient amount of the target material is produced.

In a method for simultaneously reacting the above tertiary amine derivatives, epihalohydrin, and fatty acid, the reaction temperature is between 60 to 120°C and the reaction time is from 5 to 30 hours, and a reaction solvent can be either used or not used. Examples of solvents which can be
25 employed as reaction solvents include water, methanol, ethanol, 1-propanol, 1-butanol, 2-propanol, ethyleneglycol, glycerin, propyleneglycol, polyethyleneglycol, univalent, bivalent, trivalent, polyvalent alcohols, etc. The consumed amount of the reaction solvent is from 10 to 100 wt% of the total reactant amount.

30 [EXAMPLES]

Preferred EXAMPLES are described below to help in understanding

the present invention. However, the following EXAMPLES are provided only to explain the present invention more fully, and the present invention is not restricted to the following EXAMPLES.

EXAMPLE 1

5 Lauryl amido propyl dimethyl amine, tertiary amine containing amide group, was prepared by amidation reacting 156 g of dimethylaminopropylamine (1.53 mol, 2% excess) and 300 g of lauric acid (1.5 mol) at a temperature of 140 to 145°C and a pressure of 3 to 4 atmospheres for 18 hours in a four-neck flask in which a mechanical agitator, thermometer,
10 and condenser are mounted. The measured amine value was 101.6% and an acid value was 5.9%. The resulting material of the amidation reaction was then dissolved in acetone, cooled, crystallized, filtered, and dried. Next, the above prepared 100 g of laurylamidopropyldimethyl amine (0.352 mol) were placed in a reactor, following the simultaneous placing therein of 84.5 g of
15 lauric acid (0.423 mol, 20% excess) and 39.1 g of epichlorohydrin (0.423 mol, 20% excess). Subsequently, as a solvent, 96 g of 2-propanol (30 wt% of the total reactant) were added to the reactor and reacted therein at a temperature of 90 to 95°C for 23 hours. After the reaction, a product yield of over 95% was calculated from the remaining amine and acid content by measuring an
20 amine value and an acid value using the Korean Standard analysis method. When this product was dissolved into acetone and then cooled, crystals were formed. The crystals were filtered and then underwent the procedure of again being dissolved in acetone, cooled, crystallized and filtered two more times. The resulting material was then dried to obtain the pure cationic
25 surfactant of EXAMPLE 1 in a powder form. The ultimate biodegradability of this powder was evaluated.

EXAMPLE 2

Using the same equipment as in EXAMPLE 1, 89 g of N,N-dimethylethanolamine (1.0 mol), 200 g of lauric acid (1.0 mol), and 92.5 g of
30 epichlorohydrin (1.0 mol) were simultaneously put into a reactor, and then, as a solvent, 163 g of 2-propanol (30 wt% of the total reactant) were added

thereto and reacted at a temperature of 70 to 80°C for 26 hours. After the reaction, a product yield of over 95% was calculated from the remaining amine and acid content by measuring an amine value and an acid value using the Korean Standard analysis method. After the 2-propanol, which was used as a solvent, was removed from this reactant, the reactant was dissolved in ethyl ether and cooled, thereby forming crystals which were then filtered. When the solvent was removed by drying the crystals under reduced pressure, and the pure paste-type cationic surfactant of EXAMPLE 2 was obtained. The ultimate biodegradability of this paste was evaluated.

10 EXAMPLE 3

After installing a distiller on the same equipment as used in EXAMPLE 1, N,N-dimethylaurylesteramine, tertiary amine containing ester group, was prepared by reacting 356.6 g of N,N-dimethylethanolamine (4.0 mol, 2 equivalent) and 400 g of lauric acid (2.0 mol) at a temperature of 170 to 180°C for 13 hours using 1.5 g of hypophosphorous acid (50% water solution) as a catalyst. At this time, water which was produced from the reaction and excess amine were removed using the distiller. The starting amine was used in subsequent reactions after it was removed by washing it twice with water after the reaction. The acid value of the above tertiary amine containing ester group, N,N-dimethylaurylesteramine, was 0.2%. Next, the above prepared 200 g of N,N-dimethylaurylesteramine (0.738 mol), 177 g of lauric acid (0.885 mol, 20% excess), and 81.9 g of epichlorohydrin (0.885 mol, 20% excess) were simultaneously put into a reactor using the same equipment as in EXAMPLE 1. Subsequently, 197 g of 2-propanol (30 wt% of the total reactant), used as a solvent, were added to the reactor and reacted at a temperature of 90 to 95°C for 24 hours. After the reaction, a product yield of over 90% was calculated from the remaining amine and acid content by measuring an amine value and an acid value using the Korean Standard analysis method. After the 2-propanol, which was used as a solvent, was removed from this product, the product was dissolved in acetone and cooled, thereby forming crystals. The crystals were filtered and then underwent the

procedure of again being dissolved in acetone, cooled, crystallized and filtered two more times. The resulting material was then dried to obtain the pure cationic surfactant of EXAMPLE 3 in a white powder form. The ultimate biodegradability of this powder was evaluated.

5 EXAMPLE 4

Using the same equipment as in EXAMPLE 3, N,N-dimethylmyristylesteramine, tertiary amine containing ester group, was prepared by reacting 58.6 g of N,N-dimethylethanolamine (0.66 mol, 1.5 equivalent) and 100 g of myristic acid (0.44 mol) at a temperature of 160 to 10 170°C for 15 hours using 0.3 g of hypophosphorous acid (50% water solution) as a catalyst. After the reaction, the starting amine was used in subsequent reactions after it was removed under reduced pressure. Next, the above prepared N,N-dimethylmyristylesteramine, 100 g of myristic acid (0.44 mol), and 41 g of epichlorohydrin (0.44 mol) were simultaneously put into a reactor 15 using the same equipment as in EXAMPLE 1. Subsequently, 110 g of 2-propanol (30 wt% of the total reactant), used as a solvent, were added to the reactor and reacted at a temperature of 90 to 95°C for 24 hours. After the reaction was finished, a product yield of over 90% was calculated from the remaining amine and acid content by measuring an amine value and an acid 20 value using the Korean Standard analysis method. After the 2-propanol, which was used as a solvent, was removed from this product, the product was dissolved in acetone and cooled, thereby forming crystals. The crystals were filtered and then underwent the procedure of again being dissolved in acetone, cooled, crystallized and filtered two more times. The resulting material was 25 then dried to obtain the pure cationic surfactant of EXAMPLE 4 in a white powder form. The ultimate biodegradability of this powder was evaluated.

EXAMPLE 5

Using the same equipment as in EXAMPLE 3, N,N-dimethylpalmitilesteramine, tertiary amine containing ester group, was 30 prepared by reacting 52.1 g of N,N-dimethylethanolamine (0.59 mol, 1.5 equivalent) and 100 g of palmitic acid (0.39 mol) at a temperature of 160 to

170°C for 15 hours using 0.3 g of hypophosphorous acid (50% water solution) as a catalyst. After the reaction was finished, starting amine was used in subsequent reactions after it was removed under reduced pressure. Next, the above prepared N,N-dimethylpalmitilesteramine, 100 g of palmitic acid (0.39 mol), and 36.1 g of epichlorohydrin (0.39 mol) were simultaneously put into a reactor using the same equipment as in EXAMPLE 1. Subsequently, 110 g of 2-propanol (30 wt% of the total reactant), used as a solvent, were added to the reactor and reacted at a temperature of 90 to 95°C for 24 hours. After the reaction was finished, a product yield of over 90% was calculated from the remaining amine and acid content by measuring an amine value and an acid value using the Korean Standard analysis method. After the 2-propanol, which was used as a solvent, was removed from this product, the product was dissolved in acetone and cooled, thereby forming crystals. The crystals were filtered and then underwent the procedure of again being dissolved in acetone, cooled, crystallized and filtered twice. The resulting material was then dried to obtain the pure cationic surfactant of EXAMPLE 5 in a white powder form. The ultimate biodegradability of this powder was evaluated.

EXAMPLE 6

Using the same equipment as in EXAMPLE 3, N,N-dimethylstearylesteramine, tertiary amine containing ester group was prepared by reacting 47 g of N,N-dimethylethanolamine (0.53 mol, 1.5 equivalent) and 100 g of stearic acid (0.35 mol) at a temperature of 160 to 170°C for 15 hours using 0.3 g of hypophosphorous acid (50% water solution) as a catalyst. After the reaction was finished, starting amine was used in subsequent reactions after it was removed under reduced pressure. Next, the above prepared N,N-dimethylstearylesteramine, 100 g of stearic acid (0.35 mol), and 32.4 g of epichlorohydrin (0.35 mol) were simultaneously put into a reactor using the same equipment as in EXAMPLE 1. Subsequently, 100 g of 2-propanol (30 wt% of the total reactant), used as a solvent, were added to a reactor and reacted at a temperature of 90 to 95°C for 24 hours. After the

reaction was finished, a product yield of over 90% was calculated from the remaining amine and acid content by measuring an amine value and an acid value using Korean Standard analysis method. After the 2-propanol, which was used as a solvent, was removed from this product, the product was dissolved in acetone and cooled, thereby forming crystals. The crystals were filtered and then underwent the procedure of again being dissolved in acetone, cooled, crystallized and filtered two more times. The resulting material was then dried to obtain the pure cationic surfactant of EXAMPLE 6 in a white powder form. The ultimate biodegradability of this powder was evaluated.

10 EXAMPLE 7

Using the same equipment as in EXAMPLE 3, N,N-dimethylstearylesteramine, tertiary amine containing ester group, was prepared by reacting 32.6 g of N,N-dimethylethanolamine (0.37 mol, 2.0 equivalent) and 50 g of a mixed fatty acid of stearic acid and palmitic acid (0.18 mol), in which the ratio of stearic acid to palmitic acid is 7 to 3, at a temperature of 160 to 170°C for 20 hours using 0.16 g of hypophosphorous acid (50% water solution) as a catalyst. After the reaction was finished, starting amine was used in subsequent reactions after it was removed under reduced pressure. Next, the above prepared 38.5 g of N,N-dimethylstearylesteramine (0.11 mol), 30.5 g of stearic acid (0.11 mol), and 10.35 g of epichlorohydrin (0.11 mol) were simultaneously put into a reactor using the same equipment as in EXAMPLE 1. Subsequently, 9 g of 2-propanol (10 wt% of the total reactant), used as a solvent, were added to the reactor and reacted at a temperature of 90 to 95°C for 12 hours. After the reaction was finished, a product yield of over 90% was calculated from the remaining amine and acid content by measuring an amine value and an acid value using the Korean Standard analysis method. After the non-reacted amine was neutralized with 1.74 g of hydrochloric acid (35%), the 2-propanol, which was used as a solvent, was removed from this product, and the cationic surfactant of EXAMPLE 7 was obtained. The ultimate biodegradability of the cationic surfactant was evaluated using this.

EXAMPLE 8

Using the same equipment as in EXAMPLE 1, N,N-dimethylstearylesteramine, tertiary amine containing ester group, was prepared by reflux reacting 36.6 g of N,N-dimethylethanolamine (0.41 mol) and 100 g of a mixed fatty acid of stearic acid and palmitic acid (0.37 mol), in which the ratio of stearic acid to palmitic acid is 7 to 3, at a temperature of 125 to 130°C for 20 hours using 0.27 g of hypophosphorous acid (50% water solution) as a catalyst. 50% of the non-reacted fatty acid remained at the time when there was no longer any reaction. Next, the above prepared 45 g of N,N-dimethylstearylesteramine, 45 g of stearic acid (0.17 mol), and 35 g of epichlorohydrin (0.38 mol) were simultaneously put into a reactor. Subsequently, 25 g of 2-propanol (10 wt% of the total reactant), used as a solvent, were added to the reactor and reacted at a temperature of 90 to 95°C for 5 hours. After the reaction was finished, a product yield of over 90% was calculated from the remaining amine and acid content by measuring an amine value and an acid value using the Korean Standard analysis method. After non-reacted amine was neutralized with 4.0 g of hydrochloric acid (35%), the 2-propanol, which was used as a solvent, was removed from this product, and the cationic surfactant of EXAMPLE 8 was obtained. The ultimate biodegradability of the cationic surfactant was evaluated.

[TEST EXAMPLE]

Evaluation of ultimate biodegradability

Measuring of the ultimate biodegradability was made by taking an OECD 301D Closed Bottle Test (a test for determining whether or not 60% or more can be biodegraded two weeks from the time when the sample begins decomposing during the test period of 28 days) on cationic surfactants prepared in EXAMPLES 1 to 8, dimethyl dialkyl ammonium chloride, and imidazoline ester. The results of the ultimate biodegradabilities are represented in Table 1. The ultimate biodegradabilities of cationic surfactants of EXAMPLE 1, 2, 8, and conventional cationic surfactants were less than 60%, thereby not being readily biodegradable. On the other hand, ultimate

biodegradabilities of cationic surfactants of EXAMPLES 3 to 7 were more than 60%, indicating that these surfactants are readily biodegradable.

[Table 1] Results of ultimate biodegradability *evaluations

EXAMPLES	Readily biodegradable
EXAMPLE 1	No
EXAMPLE 2	No
EXAMPLE 3	Yes
EXAMPLE 4	Yes
EXAMPLE 5	Yes
EXAMPLE 6	Yes
EXAMPLE 7	Yes
EXAMPLE 8	No
Dimethyl dialkyl ammonium chloride	No
Imidazoline ester ammonium salt	No

- 5 (*Ultimate biodegradability is a test for evaluating a degree of which test samples are completely biodegraded into water and carbon dioxide)

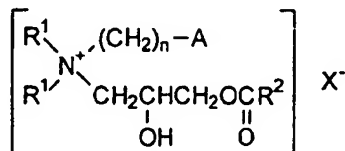
The present invention is characterized in that a cationic surfactant with a high yield is easily obtained by reacting tertiary amine derivatives, fatty acid, and epihalohydrin in one step. A cationic surfactant, which has excellent
10 physical chemical characteristics such as softness, antistatic properties, etc. as well as biodegradability due to its having an ester group and hydrophilic hydroxyl group in its molecules, can be synthesized with a high degree of purity.

While the present invention has been described in detail with
15 reference to the preferred examples, those skilled in the art will appreciate that various modifications and substitutions can be made thereto without departing from the spirit and scope of the present invention as set forth in the appended claims.

WHAT IS CLAIMED IS:

1. A method for preparing a cationic surfactant of the following General Formula 1 comprising the step of reacting tertiary amine derivatives, fatty acid, and epihalohydrin:

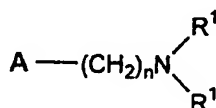
5 [General Formula 1]



wherein R¹ is a C₁ – C₄ alkyl group; R² is a C₇ – C₂₁ linear or branched alkyl or alkenyl group; A is OCOR³, NHCOR³ or OH; R³ is a C₇ – C₂₁ linear or branched alkyl or alkenyl group; X is a halogen atom; and n is an integral number from 2
10 to 6.

2. A preparation method in accordance with claim 1, wherein the tertiary amine derivatives are represented in the following General Formula 2:

[General Formula 2]



15 wherein R¹ is a C₁ – C₄ alkyl group; A is OCOR³, NHCOR³ or OH; R³ is a C₇ – C₂₁ linear or branched alkyl or alkenyl group; and n is an integral number from 2 to 6.

3. A preparation method in accordance with claim 1, wherein the fatty acid is a mixture comprising more than one compound having a C₈ – C₂₂
20 linear or branched alkyl group or alkenyl group.

4. A preparation method in accordance with claim 1, wherein the fatty acid uses from 0.8 to 1.3 equivalent tertiary amine derivative.

5. A preparation method in accordance with claim 1, wherein the epihalohydrin uses from 1.0 to 1.3 equivalent tertiary amine derivative.

25 6. A preparation method in accordance with claim 1, wherein a reaction temperature is from 60 to 120°C.

7. A preparation method in accordance with claim 1, wherein a reaction time is from 5 to 30 hours.

8. A preparation method in accordance with claim 1, wherein a reaction solvent is selected from a group comprised of water, methanol, ethanol, 1-propanol, 1-butanol, 2-propanol, ethyleneglycol, glycerin, propyleneglycol, polyethyleneglycol, univalent, bivalent, trivalent, and polyvalent alcohols.

9. A preparation method in accordance with claim 1, wherein the solvent is from 10 to 100 wt% of total reactant amount.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 99/00407

A. CLASSIFICATION OF SUBJECT MATTER IPC ⁷ : C 11 D 1/62; C 07 C 213/02; C 07 C 217/28 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC ⁷ : C 11 D; C 07 C Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPODOC, WPI, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 06-199748 (TOHO CHEM IND CO LTD) 19 July 1994 (19.07.94) (abstract). World Patent Index [online]. London, U.K.:Derwent publications Ltd. [retrieved on 03 November 1999 (03.11.99)]. Retrieved from: EPO Database., DW 199422, Accession No. 1994-269397(33).	1-9
A	GB 1386855 A (WESTVACO CORPORATION) 12 March 1975 (12.03.75). see reaction I and II (on page 2).	1-5
A	WO 94/07978 A1 (Henkel Kommanditgesellschaft auf Aktien) 14 April 1994 (14.04.94) see formula I; claims 1-9 (Cited in the application).	1-5

<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: „A“ document defining the general state of the art which is not considered to be of particular relevance „E“ earlier application or patent but published on or after the international filing date „L“ document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) „O“ document referring to an oral disclosure, use, exhibition or other means „P“ document published prior to the international filing date but later than the priority date claimed „T“ later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention „X“ document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone „Y“ document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art „&“ document member of the same patent family		
Date of the actual completion of the international search <div style="text-align: center; padding-top: 10px;">03 November 1999 (03.11.99)</div>		Date of mailing of the international search report <div style="text-align: center; padding-top: 10px;">06 December 1999 (06.12.99)</div>
Name and mailing address of the ISA/AT Austrian Patent Office Kohlmarkt 8-10; A-1014 Vienna Facsimile No. 1/53424/200		Authorized officer <div style="text-align: center; padding-top: 10px;">Dr. E. Seirafi</div> Telephone No. 1/53424/224

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR 99/00407

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche		Datum der Veröffentlichung Publication date Date de publication		Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets		Datum der Veröffentlichung Publication date Date de publication	
JJ	6199748			keine - none - rien			
JP A2	6199748	19-07-1994		keine - none - rien			
GB A	1386855	12-03-1975	CA A1	983482		10-02-1976	
			DE A	2218144		02-11-1972	
			DE B2	2218144		28-05-1975	
			DE C3	2218144		22-01-1976	
			JP B4	53023347		14-07-1978	
			US A	3718639		27-02-1973	
			CA A1	985114		09-03-1976	
			US A	3871893		18-03-1975	
WD A1	9407878	14-04-1994	AT E	147735		15-02-1997	
			AU B2	689081		26-03-1998	
			CN A	1087905		15-06-1994	
			CZ A3	9500842		13-09-1995	
			CZ B6	283362		18-03-1998	
			DE C0	69307527		27-02-1997	
			DE T2	69307527		22-05-1997	
			DK T3	663907		03-02-1997	
			EP A1	663907		26-07-1995	
			EP B1	663907		15-01-1997	
			ES T3	2096329		01-03-1997	
			FI A	951591		04-04-1995	
			FI A0	951591		04-04-1995	
			FR A1	2696459		08-04-1994	
			FR B1	2696459		25-11-1994	
			GR T3	3022285		30-04-1997	
			HU A0	9500967		28-06-1995	
			HU A2	72612		28-05-1995	
			JP T2	8301789		27-02-1996	
			LT A	1396		31-01-1995	
			LT B	3439		25-10-1995	
			LV A	10858		20-10-1995	
			LV B	10858		20-02-1996	
			MX A1	9305767		31-05-1994	
			NO A	951202		29-03-1995	
			NO A0	951202		29-03-1995	
			NZ A	256446		25-06-1996	
			PL A1	308306		24-07-1995	
			SG A1	63619		30-03-1999	
			SK A3	435795		09-08-1995	
			US A	5637723		10-06-1997	
			ZA A	9307319		22-04-1994	